CH 335

Final Exam

Thursday, March 20, 2014

Name\_\_\_\_\_

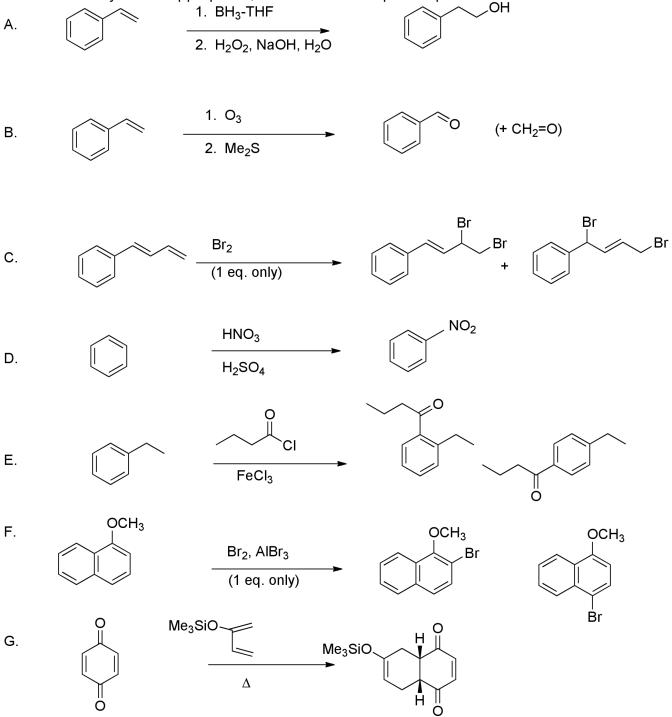
You may use model kits but no other material with chemical information without instructor approval.

Please do not use ipods or other music players.

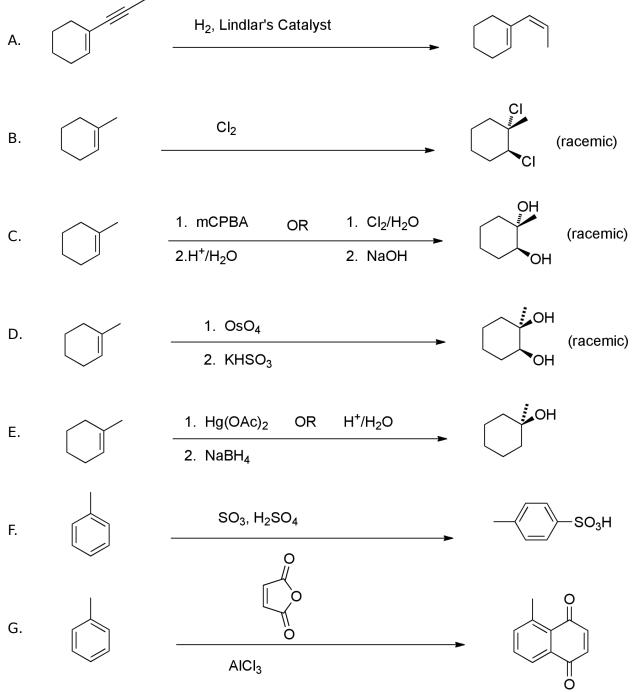
hydrogen 1																	2005 3	hellum 2
Ĥ																		He
1.0079 lithium 3	beryllium <b>4</b>											Ī	boron 5	carbon 6	nitrogen 7	oxygen 8	fluorine 9	4.0026 neon 10
Li	Be												В	С	Ν	0	F	Ne
6.941 sodium	9.0122 magnesium												10.811 aluminium	12.011 silicon	14.007 phosphorus	15.999 sulfur	18.998 chlorine	20.180 argon
11	12												13	14	15	16	17	18
Na	Mg												AI	Si	P	S	CI	Ar
22.990	24.305 calcium		scandium	titanium	vanadium	a han an is ma	0000000000	leen	askall	nickel	000001	in la la	26.982	28.086	30.974	32.065 selenium	35.453 bromine	39.948
potassium 19	20		21	22	23	chromium 24	manganese 25	iron 26	cobalt 27	28	copper 29	zinc 30	gallium 31	germanium 32	arsenic 33	34	35	krypton 36
ĸ	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
39.098	40.078		44.956	47.867	50.942	51.996	54.938	55.845	58.933	58.693	63.546	65.39	69.723	72.61	74.922	78.96	79.904	83.80
rubidium 37	strontium 38		yttrium 39	zirconium 40	niobium 41	molybdenum 42	technetium 43	ruthenium 44	rhodium 45	palladium 46	silver 47	cadmium 48	indium 49	tin 50	antimony 51	tellurium 52	iodine 53	xenon 54
Rb	Sr		V	Žr	Nb	Мо	Tc	Ru	Rh	Pd		Cd	În	Sn	Sb	Te	35 	Xe
85.468	87.62		88,906	91.224	92,906	95,94	[98]	101.07	102.91	106.42	<b>Ag</b>	112.41	114.82	118.71	121.76	127.60	126.90	131.29
caesium	barium	1000000	lutetium	hafnium	tantalum	tungsten	rhenium	osmium	iridium	platinum	gold	mercury	thallium	lead	bismuth	polonium	astatine	radon
55	56	57-70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	*	Lu	Hf	Та	W	Re	Os	lr	Pt	Au	Hg		Pb	Bi	Po	At	Rn
132.91	137.33		174.97	178.49	180.95	183.84	186.21	190.23	192.22	195.08	196.97	200.59	204.38	207.2	208.98	[209]	[210]	[222]
francium 87	radium 88	89-102	lawrencium 103	rutherfordium 104	dubnium 105	seaborgium 106	bohrium 107	hassium 108	meitnerium 109	ununnilium 110	unununium 111	ununbium 112		ununquadium 114				
Fr	Ra	* *	Lr	Rf	Db	Sg	Bh	Hs	Mt		Uuu			Uuq				
[223]	[226]		[262]	[261]	[262]	[266]	[264]	[269]	[268]	[271]	[272]	[277]		12891				

*Lanthanide series	lanthanum 57	cerium 58	praseodymium 59	neodymium 60	promethium 61	samarium 62	europium 63	gadolinium <b>64</b>	terbium 65	dysprosium 66	holmium 67	erbium 68	thulium 69	ytterbium 70
Lanthaniue Series	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
	138.91	140.12	140.91	144.24	[145]	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.04
	actinium	thorium	protactinium	uranium	neptunium	plutonium	americium	curium	berkelium	californium	einsteinium		mendelevium	nobelium
* * Actinide series	89	90	91	92	93	94	95	96	97	98	99	100	101	102
	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
	[227]	232.04	231.04	238.03	[237]	[244]	[243]	[247]	[247]	[251]	[252]	[257]	[258]	[259]

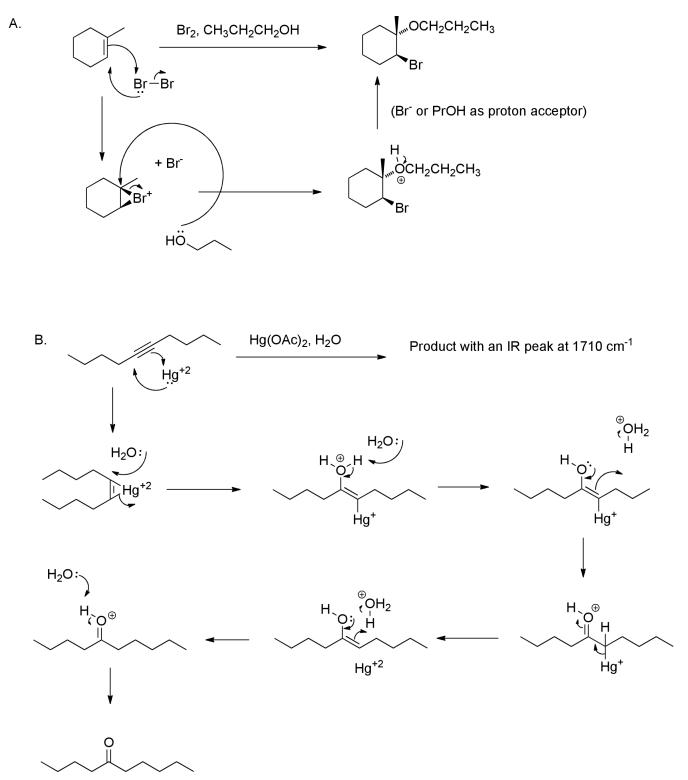
1. (35 points) Write the expected product(s) for each of the following reactions. Specify stereochemistry where appropriate, and include all expected products.

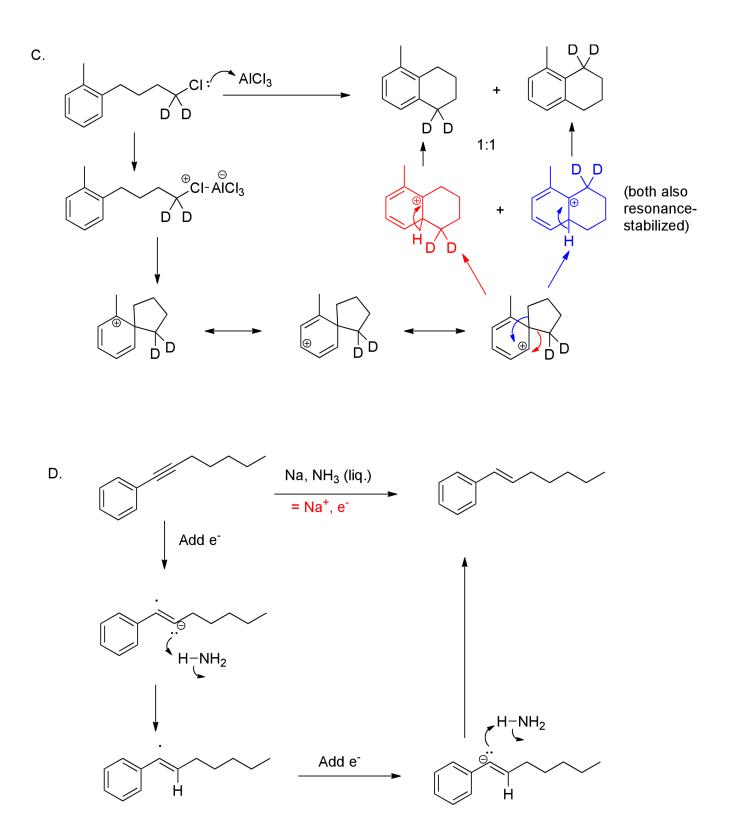


2. (35 points) Write (over the arrow) the reagents and/or conditions needed to accomplish the following transformations.



3. (28 points) Write multistep mechanisms (using the correct electron-pushing formalism, and as many steps as needed) for each of the following transformations. Be sure to draw resonance structures for any intermediate so stabilized.



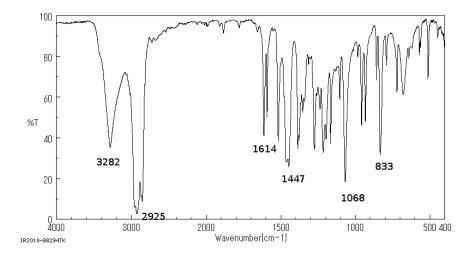


4. (25 points) A molecule has the molecular formula  $C_8H_{10}O_2$ .

A. How many degrees of unsaturation does it have?

 $(2 \times 8 (\#C) + 2 - 10 (\# H))/2 = 4$ 

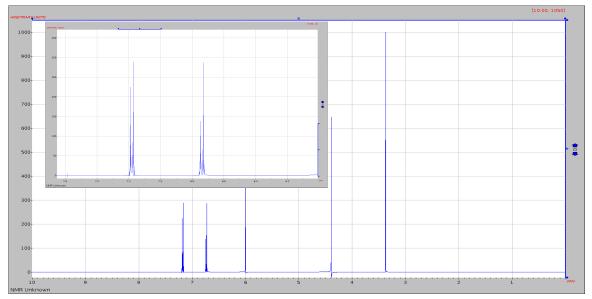
B. The infrared spectrum is shown below. Circle any peaks that tell you what functional groups are present, and list those functional groups. Several peaks are identified to help you estimate the scale.



3282: O-H (sharper than normal, but the other alternative—N-H—is not possible because of the molecular formula.)

2925: C-H.

C. The <sup>1</sup>H NMR with expansion (6-7.5 ppm) is shown below; integrations are listed below the spectrum. Propose a structure that is consistent with all this data. (Failing a complete structure, suggest what fragments are present for partial credit.)

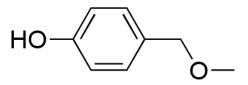


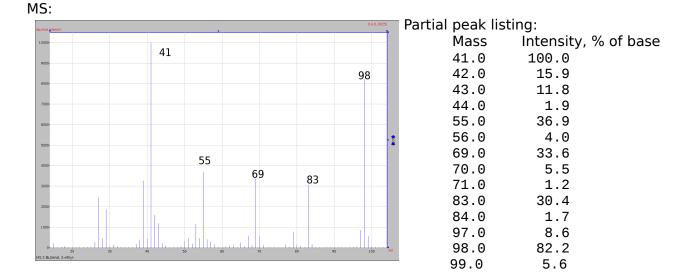
Integrals: 7.18 ppm: 2H 6.74 ppm: 2H 6.00 ppm: 1H 4.39 ppm: 2H 3.37 ppm: 3H

4 DoU suggests an aromatic compound, confirmed by the two doublets in the aromatic region (6.74/7.18). Because we see two doublets (2H each) this must be a para-disubstituted benzene.

Since we know we have an OH from the IR, we can assign this to the 1H signal at 6.00 ppm.

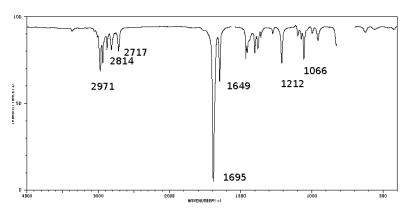
The other two signals, a  $CH_3$  and a  $CH_2$  group, are both fairly far downfield—the  $CH_2$  moreso than the  $CH_3$ . We have a second oxygen to explain, as well. If both are bonded to the second oxygen, everything fits. The two benzene substituents are -OH and -CH<sub>2</sub>OCH<sub>3</sub>.



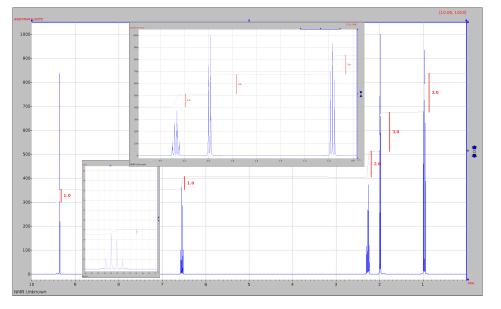


5. (25 points) The mass, IR, <sup>1</sup>H and <sup>13</sup>C NMR spectra for a compound are shown below.

IR:



<sup>1</sup>H NMR (insets are 0.5-2.5 ppm above; 6.2-6.8 ppm below):



Integrals:

9.36 ppm 1H 6.55 ppm 1H 2.27 ppm 2H 1.99 ppm 3H

0.97 ppm 3H

<sup>13</sup>C NMR:

194.84 149.42 146.38 16.96 14.51 12.99

(continued next page)

A. From the mass spectrum (and clues in other spectra), deduce the molecular formula.

The parent ion at 98 has an (M+1) peak that is 6.6% as intense—so 6 carbons (72 mass units). There is a C=O evident in the IR, so there must be oxygen (16 more mass units—total 88). By difference, there are 10 hydrogens, and this matches the total integration in the <sup>1</sup>H NMR.

## C<sub>6</sub>H<sub>10</sub>O

B. Propose a structure that fits the data. (If you cannot come up with a complete structure, provide as much analysis of the data as you can.) Be sure to:

-Calculate the degrees of unsaturation

-Specify functional groups, the evidence you use to identify them, and the impact on the DoU count

-Identify coupling relationships that allow you to identify structural pieces -Any corroborating evidence you can see that confirms the structure.

2 degrees of unsaturation; one of these is the C=O seen in the IR.

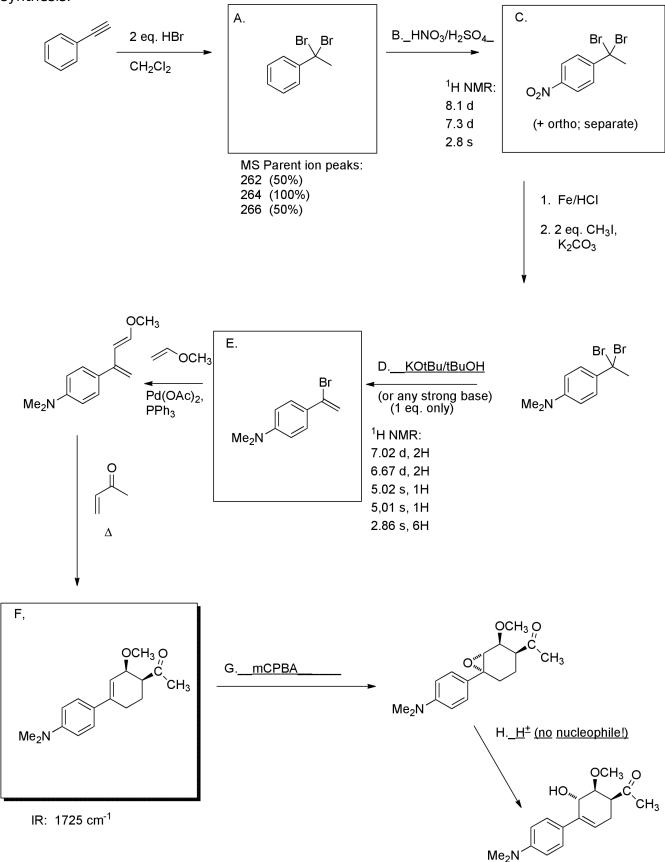
Looking at the 13C NMR, we also see (in addition to the C=O at 194.84 ppm) two carbons in the  $sp^2$  region (149.42, 146.38), so there is a C=C double bond and no ring.

The <sup>1</sup>H NMR shows us one vinyl C-H proton (6.55 ppm) only, so the double bond is trisubstituted. This is a quartet, so there is a  $CH_3$  group on the double bond, confirmed by a quartet at 1.99 ppm (in the right chemical shift area, too).

The remaining <sup>1</sup>H NMR signals are at 9.36: a 1-H singlet; this tells us we have an aldehyde as one substituent on the double bond (uncoupled to any other hydrogens). The remaining signals—a 2-H quartet and a 3-H triplet—are signatures for an ethyl group.

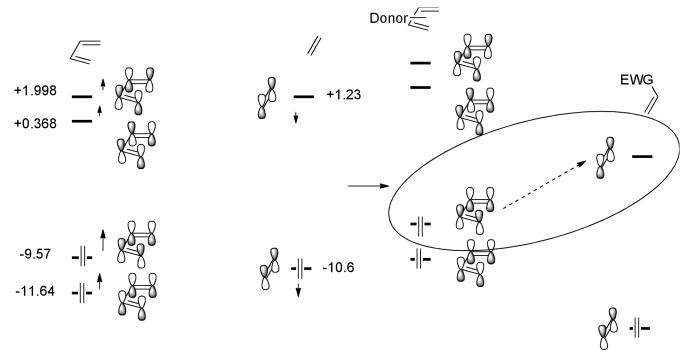
Could be E or Z--no way to distinguish with our data)

6. (32 points) Fill in the missing intermediates or reagents in the following multistep synthesis.



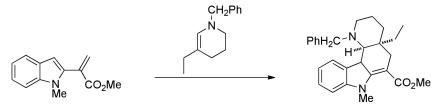
7. (20 points) Normally, the Diels-Alder reaction involves a diene with an electron-donating group reacting with a dienophile that has an electron-withdrawing substituent.

A. Based on the MO diagram below depicting the orbitals in the unsubstituted case (and their energies, in eV), describe why this particular pair of substituents enhances the Diels-Alder reaction. Use the molecular orbital description of the bonding in the reactants and the transition state.



An electron donating group will shift the energies of the diene MOs UP because of destabilization due to electron-electron repulsion. An electron-withdrawing group will move the MOs of the dienophile DOWN, moving the LUMO closer to the energy of the diene HOMO.

B. There are examples of what are called "inverse demand" Diels-Alder reactions, where the electron donor is on the dienophile, and the electron-withdrawing group is on the diene. An example is shown:



In the diagram below, shade in the phases of the orbitals to represent the major HOMO-LUMO interaction in the transition state for this inverse-demand Diels-Alder reaction. (Hint: think about how you would adapt your answer to Part A to explain what happens here.)

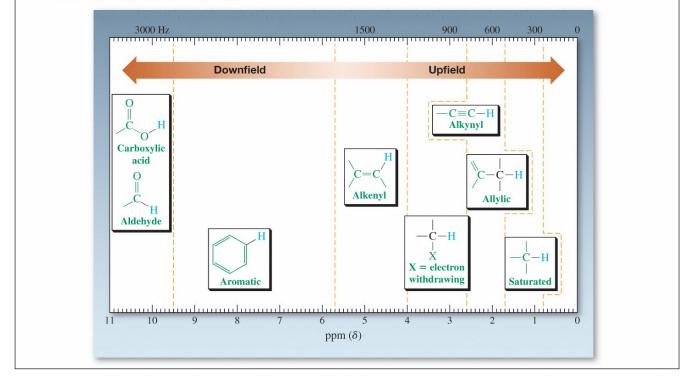


The reverse would happen here: the diene MOs will be stabilized, and the alkene MO's pushed up. The best interaction will be the diene LUMO interacting with the dienophile HOMO.

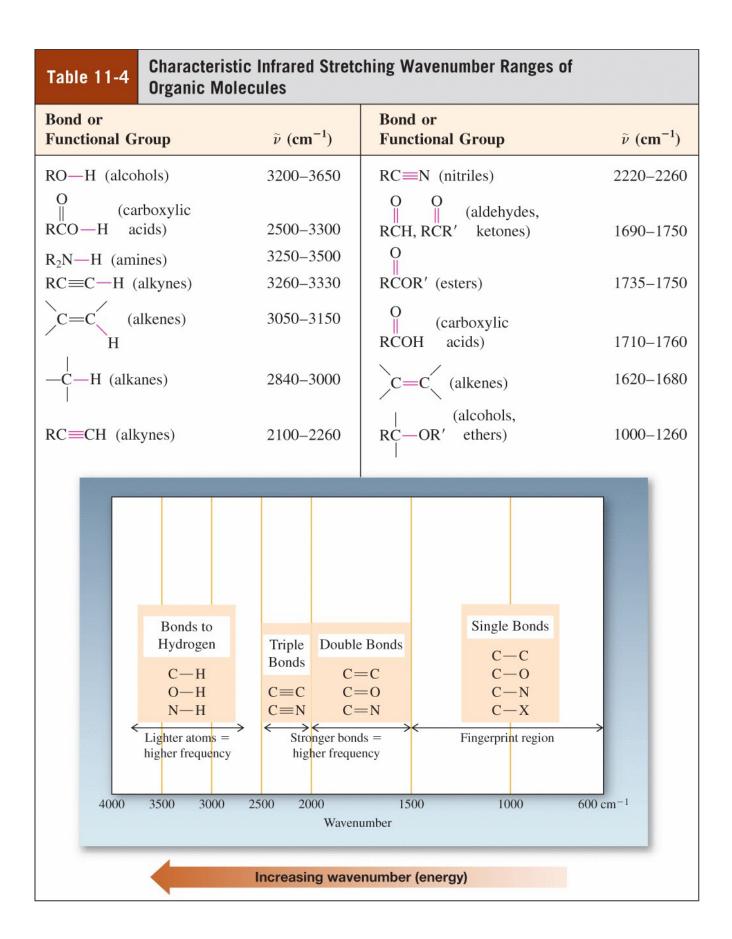
EWG = Electron-Withdrawing Group EDG = Electron-Donating Group

Table 10-2         Typical Hydrogen Chemical Shifts in the second se	Organic Molecules	
Type of hydrogen <sup>a</sup>		Chemical shift $\delta$ in ppm
Primary alkyl, RCH <sub>3</sub>	0.8-1.0	
Secondary alkyl, RCH <sub>2</sub> R'	1.2–1.4	Alkane and alkane-like hydrogens
Tertiary alkyl, R <sub>3</sub> CH	1.4–1.7 J	
CH <sub>3</sub>		
Allylic (next to a double bond), $R_2C = C$	1.6-1.9	
R'		
Benzylic (next to a benzene ring), ArCH <sub>2</sub> R	2.2-2.5	Hydrogens adjacent to unsaturated functional groups
Ketone, RCCH <sub>3</sub>	2.1-2.6	
0		
Alkyne, RC≡CH	1.7–3.1	
Chloroalkane, RCH <sub>2</sub> Cl	3.6-3.8	
Bromoalkane, RCH <sub>2</sub> Br	3.4–3.6	
Iodoalkane, RCH <sub>2</sub> I	3.1–3.3	Hydrogens adjacent to electronegative atoms
Ether, $RCH_2OR'$	3.3-3.9	
Alcohol, $RCH_2OH$	3.3–4.0 J	
Terminal alkene, $R_2C = CH_2$	4.6–5.0	Alkene hydrogens
Internal alkene, $R_2C = CH$	5.2-5.7	Timone nyurogens
R'		
Aromatic, ArH	6.0-9.5	
Aldehyde, RCH	9.5-9.9	
U O		
Alcoholic hydroxy, ROH	0.5-5.0	(variable)
Thiol, RSH	0.5-5.0	(variable)
Amine, RNH <sub>2</sub>	0.5-5.0	(variable)
<sup><i>a</i></sup> R, R', alkyl groups; Ar, aromatic group (not argon).		

<sup>a</sup>R, R', alkyl groups; Ar, aromatic group (not argon).



Type of carbon	Chemical shift $\delta$ (ppm)
Primary alkyl, RCH <sub>3</sub>	5–20
Secondary alkyl, RCH <sub>2</sub> R'	20-30
Tertiary alkyl, R <sub>3</sub> CH	30-50
Quaternary alkyl, R <sub>4</sub> C	30-45
Allylic, $R_2C = CCH_2R'$	20-40
 R″	
Chloroalkane, RCH <sub>2</sub> Cl	25-50
Bromoalkane, RCH <sub>2</sub> Br	20-40
Ether or alcohol, $RCH_2OR'$ or $RCH_2OH$	50-90
Carboxylic acids, RCOOH	170-180
O O 	
Aldehyde or ketone, $\mathbf{RCH}$ or $\mathbf{RCR}'$	190–210
Alkene, aromatic, $R_2C = CR_2$	100–160
Alkyne, $RC \equiv CR$	65–95
$\begin{array}{c c} R \\ \hline \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	$\begin{array}{c} RCH_2Br \\ RCH_2Cl \\ RCH_2OR' \text{ or } \\ RCH_2OH \\ R'' \\ R_4C \\ R_3CH \end{array}$
220 210 200 190 180 170 160 150 140 130 120 F	$RC \equiv CR$ $RCH_2R'$ $RCH_3$



Bond strengths (kcal/mol):

$\begin{array}{ccccc} {\rm Cl-Cl} & 58 \\ {\rm Br-Br} & 46 \\ {\rm I-I} & 36 \\ {\rm H-F} & 136 \\ {\rm H-Cl} & 103 \\ {\rm H-Br} & 87 \\ {\rm H-I} & 71 \\ {\rm CH}_3-{\rm H} & 105 \\ {\rm CH}_3{\rm CH}_2-{\rm H} & 101 \\ ({\rm CH}_3)_2{\rm CH-{\rm H}} & 98.5 \\ ({\rm CH}_3)_3{\rm C-{\rm H}} & 96.5 \\ {\rm CH}_3-{\rm F} & 110 \\ {\rm CH}_3-{\rm Cl} & 85 \\ {\rm CH}_3-{\rm Rr} & 70 \\ {\rm CH}_3-{\rm I} & 57 \\ {\rm CH}_3{\rm CH}_2-{\rm F} & 111 \\ {\rm CH}_3{\rm CH}_2-{\rm F} & 111 \\ {\rm CH}_3{\rm CH}_2-{\rm Rr} & 70 \\ {\rm CH}_3{\rm CH}_2-{\rm I} & 56 \\ ({\rm CH}_3)_2{\rm CH-{\rm F}} & 111 \\ ({\rm CH}_3)_2{\rm CH-{\rm F}} & 111 \\ ({\rm CH}_3)_2{\rm CH-{\rm F}} & 111 \\ ({\rm CH}_3)_2{\rm CH-{\rm Cl}} & 84 \\ \end{array}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$
$\begin{array}{ccccccc} H-F & 136 \\ H-Cl & 103 \\ H-Br & 87 \\ H-I & 71 \\ CH_3-H & 105 \\ CH_3CH_2-H & 101 \\ (CH_3)_2CH-H & 98.5 \\ (CH_3)_3C-H & 96.5 \\ CH_3-F & 110 \\ CH_3-Cl & 85 \\ CH_3-Br & 70 \\ CH_3-I & 57 \\ CH_3CH_2-F & 111 \\ CH_3CH_2-F & 111 \\ CH_3CH_2-Cl & 84 \\ CH_3CH_2-Br & 70 \\ CH_3CH_2-I & 56 \\ (CH_3)_2CH-F & 111 \\ \end{array}$
$\begin{array}{cccccc} H-Cl & 103 \\ H-Br & 87 \\ H-I & 71 \\ CH_3-H & 105 \\ CH_3CH_2-H & 101 \\ (CH_3)_2CH-H & 98.5 \\ (CH_3)_3C-H & 96.5 \\ CH_3-F & 110 \\ CH_3-Cl & 85 \\ CH_3-Br & 70 \\ CH_3-I & 57 \\ CH_3CH_2-F & 111 \\ CH_3CH_2-Cl & 84 \\ CH_3CH_2-Br & 70 \\ CH_3CH_2-I & 56 \\ (CH_3)_2CH-F & 111 \\ \end{array}$
$\begin{array}{ccccc} H-Br & 87 \\ H-I & 71 \\ CH_3-H & 105 \\ CH_3CH_2-H & 101 \\ (CH_3)_2CH-H & 98.5 \\ (CH_3)_3C-H & 96.5 \\ CH_3-F & 110 \\ CH_3-Cl & 85 \\ CH_3-Br & 70 \\ CH_3-I & 57 \\ CH_3CH_2-F & 111 \\ CH_3CH_2-Cl & 84 \\ CH_3CH_2-Br & 70 \\ CH_3CH_2-I & 56 \\ (CH_3)_2CH-F & 111 \\ \end{array}$
$\begin{array}{ccccc} H - I & 71 \\ CH_3 - H & 105 \\ CH_3 CH_2 - H & 101 \\ (CH_3)_2 CH - H & 98.5 \\ (CH_3)_3 C - H & 96.5 \\ CH_3 - F & 110 \\ CH_3 - Cl & 85 \\ CH_3 - Br & 70 \\ CH_3 - I & 57 \\ CH_3 CH_2 - F & 111 \\ CH_3 CH_2 - F & 111 \\ CH_3 CH_2 - Cl & 84 \\ CH_3 CH_2 - I & 56 \\ (CH_3)_2 CH - F & 111 \\ \end{array}$
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$\begin{array}{ccccc} CH_{3}CH_{2}-H & 101 \\ (CH_{3})_{2}CH-H & 98.5 \\ (CH_{3})_{3}C-H & 96.5 \\ CH_{3}-F & 110 \\ CH_{3}-Cl & 85 \\ CH_{3}-Br & 70 \\ CH_{3}-I & 57 \\ CH_{3}CH_{2}-F & 111 \\ CH_{3}CH_{2}-F & 111 \\ CH_{3}CH_{2}-Cl & 84 \\ CH_{3}CH_{2}-Br & 70 \\ CH_{3}CH_{2}-I & 56 \\ (CH_{3})_{2}CH-F & 111 \\ \end{array}$
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$\begin{array}{ccccc} (CH_3)_3C-H & 96.5 \\ CH_3-F & 110 \\ CH_3-Cl & 85 \\ CH_3-Br & 70 \\ CH_3-I & 57 \\ CH_3CH_2-F & 111 \\ CH_3CH_2-Cl & 84 \\ CH_3CH_2-Br & 70 \\ CH_3CH_2-I & 56 \\ (CH_3)_2CH-F & 111 \\ \end{array}$
$\begin{array}{ccccc} CH_3 - F & 110 \\ CH_3 - Cl & 85 \\ CH_3 - Br & 70 \\ CH_3 - I & 57 \\ CH_3 CH_2 - F & 111 \\ CH_3 CH_2 - Cl & 84 \\ CH_3 CH_2 - Br & 70 \\ CH_3 CH_2 - I & 56 \\ (CH_3)_2 CH - F & 111 \\ \end{array}$
$\begin{array}{cccc} CH_3-Cl & 85 \\ CH_3-Br & 70 \\ CH_3-I & 57 \\ CH_3CH_2-F & 111 \\ CH_3CH_2-Cl & 84 \\ CH_3CH_2-Br & 70 \\ CH_3CH_2-I & 56 \\ (CH_3)_2CH-F & 111 \\ \end{array}$
$\begin{array}{cccc} CH_3 - Br & 70 \\ CH_3 - I & 57 \\ CH_3 CH_2 - F & 111 \\ CH_3 CH_2 - Cl & 84 \\ CH_3 CH_2 - Br & 70 \\ CH_3 CH_2 - I & 56 \\ (CH_3)_2 CH - F & 111 \\ \end{array}$
$\begin{array}{cccc} CH_{3}\text{-}I & 57 \\ CH_{3}CH_{2}\text{-}F & 111 \\ CH_{3}CH_{2}\text{-}Cl & 84 \\ CH_{3}CH_{2}\text{-}Br & 70 \\ CH_{3}CH_{2}\text{-}I & 56 \\ (CH_{3})_{2}CH\text{-}F & 111 \\ \end{array}$
$\begin{array}{c} CH_3CH_2\operatorname{-}F & 111 \\ CH_3CH_2\operatorname{-}Cl & 84 \\ CH_3CH_2\operatorname{-}Br & 70 \\ CH_3CH_2\operatorname{-}I & 56 \\ (CH_3)_2CH\operatorname{-}F & 111 \end{array}$
CH <sub>3</sub> CH <sub>2</sub> -Cl         84           CH <sub>3</sub> CH <sub>2</sub> -Br         70           CH <sub>3</sub> CH <sub>2</sub> -I         56           (CH <sub>3</sub> ) <sub>2</sub> CH-F         111
$\begin{array}{ccc} CH_{3}CH_{2}-Br & 70 \\ CH_{3}CH_{2}-I & 56 \\ (CH_{3})_{2}CH-F & 111 \end{array}$
CH <sub>3</sub> CH <sub>2</sub> -I 56 (CH <sub>3</sub> ) <sub>2</sub> CH-F 111
(CH <sub>3</sub> ) <sub>2</sub> CH-F 111
(CH <sub>3</sub> ) <sub>2</sub> CH-Cl 84
(0.1.5)/2011 01
(CH <sub>3</sub> ) <sub>2</sub> CH-Br 71
(CH <sub>3</sub> ) <sub>2</sub> CH-I 56
(CH <sub>3</sub> ) <sub>3</sub> C-F 110
(CH <sub>3</sub> ) <sub>3</sub> C-Cl 85
(CH <sub>3</sub> ) <sub>3</sub> C-Br 71
(CH <sub>3</sub> ) <sub>3</sub> C-I 55

